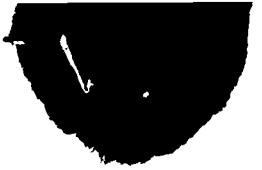


(2)

IMPLANTED CONTACTS FOR DIAMOND SEMICONDUCTOR DEVICES

FINAL REPORT

CONTRACT
DASG60-91-C-0025

SPONSORED BY

U. S. ARMY STRATEGIC DEFENSE COMMAND

CONTRACT PERIOD
2/12/91 TO 11/12/91

Soo Hee Tan and C. P. Beetz, Jr.
Principal Investigators

ADVANCED TECHNOLOGY MATERIALS, INC.
7 COMMERCE DRIVE
DANBURY, CT 06810

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION unclassified	1b. RESTRICTIVE MARKINGS None
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) N/A	5. MONITORING ORGANIZATION REPORT NUMBER(S) N/A
6a. NAME OF PERFORMING ORGANIZATION Advanced Technology Materials, Inc. 6b. OFFICE SYMBOL (*If applicable*) N/A	7a. NAME OF MONITORING ORGANIZATION U.S. Army Strategic Defense Command ATTN: CSSD-PA
6c. ADDRESS (*City, State, and ZIP Code*) 7 Commerce Drive Danbury, CT 06810	7b. ADDRESS (*City, State, and ZIP Code*) P.O. Box 1500 Huntsville, AL 35807-3801
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U.S. Army Strategic Defense Command 8b. OFFICE SYMBOL (*If applicable*)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DASG60-91-C-0025
8c. ADDRESS (*City, State, and ZIP Code*) P.O. Box 1500 Huntsville, AL 35807-3801	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (*Include Security Classification*)
Implanted Contacts for Diamond Semiconductor Devices - Unclassified

12. PERSONAL AUTHOR(S)
Soo-Hee Tan and C. P. Beetz, Jr.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (*Year, Month, Day*)	15. PAGE COUNT
Final Report	FROM 12FEB91 TO 11DEC91	92-01-27	23

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (*Continue on reverse if necessary and identify by block number*)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (*Continue on reverse if necessary and identify by block number*)

Key to future diamond semiconductor development are ohmic and Schottky contacts that are stable at high temperature. Wide bandgap materials such as diamond (5.5 eV), pose special problems and demand ingenious solutions. Prior to our work, recent research into stable ohmic and Schottky contacts had been primarily limited to e-beam evaporation of carbide forming metals such as Ti, Ta, and Mo. These approaches have been relatively successful at decreasing the specific contact resistivity to as low as 10^{-5} Ω-cm^2 on natural semiconducting diamonds with ~10^{16} boron atoms/cm^3.In our Phase I SBIR program we investigated metal systems coupled with a shallow Si implant that would form low resistivity, high temperature stable metal silicides. We showed in our Phase I results that the barrier height of metals such as Pt, Ti and Mo were reduced when deposited on shallow Si implants and given a heat treatment at 500°C. The barrier height of Pt on diamond was reduced from 1.89 eV to 0.97 eV by annealing of a sputtered Pt contact on a Si implanted dose of 10^{15} cm^{-2} that peaks at ~120Å into the diamond surface. Using the same approach, the barrier height of Ti on diamond was reduced from 2.00 eV to 1.29 eV.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ OTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL Duncan W. Brown	22b TELEPHONE (*Include Area Code*) 203-794-1100 22c OFFICE SYMBOL N/A

DD Form 1473, JUN 86 *Previous editions are obsolete* SECURITY CLASSIFICATION OF THIS PAGE

Implanted Contacts for Diamond Semiconductor Devices

TABLE OF CONTENTS

1.0 Introduction

High temperature, radiation-hardened power semiconductors are very quickly reaching their limitations. Indeed, for some applications, devices are nonexistent. There is a growing need within the DOD and throughout industry for high power semiconductor devices that are able to operate at high frequencies and power levels. Military applications for high performance power semiconductors include transport (e. g., supersonic aircraft , space based vehicles), weapons (EW, kinetic energy weapons), and communications. Commercial applications range from automobiles, to power generation, to mining and drilling operations.[1,2,3] Reliability at sustained high temperatures and radiation levels is critical. The cooling requirements of existing electronics systems and the fundamental limitations imposed by available semiconductor materials pose a significant engineering problem.

Diamond has been identified as the most promising material for these devices. It has long been known that diamond possesses the physical and electronic properties to fill the gap in high temperature, radiation hardened power semiconductor technology.

Key to future diamond semiconductor development are ohmic and Schottky contacts that are stable at high temperature. Wide bandgap materials such as diamond (5.5 eV), pose special problems and demand ingenious solutions. Prior to our work, recent research into stable ohmic and Schottky contacts had been primarily limited to e-beam evaporation of carbide forming metals such as Ti, Ta, and Mo[4,5,6]. These approaches have been relatively successful at decreasing the specific contact resistivity to as low as 10^{-5} Ω-cm^2 on natural semiconducting diamonds with ~10^{16} boron atoms/cm^3. An interesting exception is the use of a graded bandgap approach in which SiC/Si is used as a means of obtaining a smaller bandgap onto which to make ohmic contact[7]. The SiC/Si interface was produced by ion beam mixing of an evaporated Si film with the diamond surface. This lead to contacts with specific contact resistivities as low as 10^{-3} on relatively highly doped surfaces produced by implantation. Both of these approaches have the disadvantage of having an extremely high temperature heat treatments that can introduce damage in the form of sp^2 carbon to the diamond surface and introduce leakage currents. Metals beyond this limited range of carbide forming transition metals have not been well explored.

In our Phase I program we investigated metal systems coupled with a shallow Si implant that would form low resistivity, high temperature stable metal silicides. We showed in our Phase I results that the barrier height of metals such as Pt, Ti and Mo were reduced when deposited on shallow Si implants and given a heat treatment at 500°C. The barrier height of Pt on diamond was reduced from 1.89 eV to 0.97 eV by annealing of a sputtered Pt contact on a Si implanted dose of 10^{15} cm^{-2} that peaks at ~120Å into the diamond surface. Likewise using the same approach, the barrier height of Ti on diamond was reduced from 2.00 eV to 1.29 eV. Although we have no direct evidence for silicide formation at this time, the reduction of the barrier height scaled inversely to the temperature of formation of the metal silicide. This is an extremely important observation and points to the possibly of achieving very low resistance contacts. We attempted to measure the

specific contact resistivities of our contacts using a transmission line structure however the values we measured were large due to the fact that we were working on a diamond that had a very high resistivity, ~$10^{12}\Omega$-cm.

2.0 Schottky and Ohmic Contact Development Strategy for Diamond

Schottky and ohmic contact development is crucial to the success of high temperature devices. Since diamond devices are targeted for high temperature operation at 600°C or higher, Schottky and ohmic contacts must be stable to at least this temperature in terms of physical and electrical characteristics.

There have been few successes in the development of ohmic contacts for diamonds. The difficulty in the development of diamond contacts can be attributed to the fact that diamond has one of the largest bandgaps of any semiconductor material (5.5 eV). This presents a large barrier height to most metals. Thus far, limited success has been achieved with the sputtering or evaporation of Al,[8] Mo, Mo/Au, Mo/Ni/Au,[4] Ta/Au, Ti/Au,[9] Ti and W[10] systems. Other methods include producing a graphitic layer on the surface of the diamond by heating or laser damage to enhance the interaction of metals with diamond.[11,12] One method that is particularly interesting involves the reduction of the large bandgap of diamonds by using an intermediate material composed of a silicon and silicon carbide graded structure formed by ion mixing deposited silicon with the diamond surface.[7]

It has been found that the contact resistance is independent of the metal work function[13,8] and largely dependent on the metal to diamond interface.[14] Furthermore, the adhesion of as deposited metals to diamond is poor until after annealing. Even then, only those metals that react to form carbides will form stable interfaces.[4,14] For those metals that do react with carbon, the annealing temperatures needed are in excess of 1000°C. Such high annealing temperatures change the surface of diamond, forming a conductive graphitic surface. This must be removed using chromic acids which are not compatible with the processing scheme of resist and metals. The use of a converted graphite surface layer to promote interaction of metals with diamond does not produce a stable interface Such a layer is easily affected by various chemical treatments that are used in device fabrication schemes.

The most commonly used method of producing ohmic contacts in other semiconductor materials is by doping selective areas, creating a situation where with low levels of doping, thermionic emission dominates the current transport and Rc can be described by:[15]

$$R_c = \frac{k}{qTA^*}\exp\left[\frac{q\phi_B}{kT}\right] \qquad (1)$$

while for high doping concentrations, tunneling dominates and Rc can be described by :

$$R_c \approx \exp\left[\frac{2\sqrt{e_s m^* \phi_B}}{\hbar\sqrt{N_D}}\right] \qquad (2)$$

At this time, selective doping of diamond via ion implantation has not been achieved, and is proving to be difficult due to damage produced during implantation. However, some progress has been made recently using post implantation Rapid Thermal Annealing (RTA) to recrystallize the damaged region.[16,17] Non-selective doping has been achieved during diamond film deposition.

Schottky contact development is equally limited. A quick survey (table below) of the literature shows conflicting results for p-type diamonds. Thus far no data has been obtained for n-type diamonds.

Metal	ϕ_{Bp} (eV)
Au	1.73[18]
Au	1.7-2.0[19]
Au	1.25[25]
Al	1.9-2.2[25]
Al	1.0[25]
Ba	2.0[25]
Au	1.3[20]
Al	1.5[26]
Au	1.13[21]
Al	1.13[27]
Au	2.24[22]
Au	1.35[22]

Diamond is a covalent semiconductor with a heat of formation, ΔH_f of 0.4533 kcal/mole.[23] Brillson[24] has noted that there is a greater tendency for covalent compounds to form both the metal-anion as well as the metal-cation phases. It is expected that transition metals will form only carbides at the interface and these carbides will then determine to a large extent the specific contact resistivities at the iterfaces. Fang et al [25] have shown that specific contact resistivities in the order of 10^{-3} ohm-cm^2 using 240 keV Kr^+ ion to mix the deposited silicon and diamond structure to produce silicon-SiC-diamond graded structures. We propose to induce the formation of silicides at the interface by ion implantation of silicon into the diamond surface such that transition metals can be deposited and alloyed to form the intended structure. The silicide scheme is much more attractive than using doped polysilicon because most of the silicides have resistivities that are almost ten times lower than that of heavily doped polysilicon thus enabling much thinner lines to be patterned without sacrificing the speed of a device. We expect from thermodynamic considerations that the most likely

reaction at the interface will be that which has the lowest heat of reaction. The table below lists the ΔH_f(kcal/mole)[26] of some of the possible carbides and silicides for Ta, Ti, W and Fe.

Ta		Ti		W		Fe	
	ΔH_f		ΔH_f		ΔH_f		ΔH_f
TaC	-34.3	TiC	-43.9	W_2C	-6.3	Fe_3C	-6.0
Ta_2C	-48.5	Ti_5Si_3	-138.5	WC	-9.0	FeSi	-18.4
Ta_2Si	-30.0	TiSi	-31.0	WSi_2	-22.2		
Ta_5Si_3	-80.0	$TiSi_2$	-32.0	W_5Si_3	-32.3		
$TaSi_2$	-28.5						

The table below shows the metals that we proposed to investigate and their corresponding properties. We chose metals that had already been investigated by various researchers so that we could do a comparison of our techniques. In addition we investigated gold and nickel for comparison purposes.

Material	Melting pt (°C)	Resistivity (10^{-6}ohm-cm)	f_m[27] (eV)	ΔH_f[28,29] (eV/atom)
Gold	1063	2.3	5.10	
Nickel	1453	6.84	4.9	
Platinum	1769	9.8	5.65	
Tantalum	2980	13.5	4.25	
Titanium	1670	55.0	4.33	
Tungsten	3380	5.5	4.55	
Mo	2617	5.2		
PtSi	1229	28-35		0.45
$TaSi_2$	1385	50-55		3.44
$NiSi_2$	1381	50-60		1.47
$TiSi_2$	------	13-25		5.95
WSi_2	2150	70		1.39
$MoSi_2$	1410	100		1.35

We overcame the problems normally encountered in the fabrication of ohmic contacts by using the novel approach of silicon implantation into a diamond surface, then depositing a metal that can be annealed to form a silicide and carbide mixture. The reasoning behind our approach was as follows:

1. The range of ion implantation into diamonds is very well characterized and can be precisely controlled in terms of concentration and distribution. We will be investigating very shallow implantation which means that low energies will be used, thus damage to the contact surface and below will be negligible. Consequently, the electrical performances of the device will be improved.

2. Implantation of contacts is compatible with existing silicon and GaAs technologies. It can be used for the production of VLSI and self aligned technologies to reduce stray capacitances and resistances which are

deleterious to high frequency devices. Many different materials can be used for a mask since low energy silicon is being implanted.

3. The formation of a silicide/silicon carbide interface instead of a metal carbide interface will lead to a lower interface resistance. The resistivities of metal carbides are generally a few orders of magnitude higher than the corresponding silicides.

4. The formation of silicides at the interface is expected to provide a stable barrier to any further interdiffusion of the contact material and diamond.

5. With low energy shallow implantation, there is no need to recrystallize or activate the implanted ions. Rapid thermal annealing could be used to form the junction in a short time.

6. Adhesion of the metal will be improved tremendously with the silicides/metal carbide layer.

7. There is the added possibility of forming variable Schottky junctions using this approach. It is expected that depending on the dose and range of the implants, a silicon carbide layer will form if the silicon is not totally consumed by the metal. By controlling the formation of this silicon carbide layer, we should be able to control the barrier heights at the interface.

For an ideal metal to n-type semiconductor surface, the barrier height is expressed as:

$$\phi Bn = \phi m - \chi sc \qquad (3)$$

where ϕ_m is the metal work function and χ_{sc} is the electron affinity of the semiconductor measured from the bottom of the conduction band to the vacuum level. The value of the p-type barrier is simply expressed as:

$$\phi Bp = Eg/q - \phi Bn \qquad (4)$$

where Eg is the semiconductor energy gap and q is the electron charge.

However, there are no ideal interfaces, and traps at the interface will modify the barrier height. For decades, these traps have been attributed to intrinsic states at the semiconductor surface but it has been shown conclusively that intrinsic states play no role in barrier formation.[30] Instead, the barrier height is dependent on the interaction between the semiconductor and metal in the following manner.

1. Metals can be classified into reactive and unreactive by the interface heats of reaction, ΔH_R. The more negative ΔH_R, the more reactive the metal is at the interface and the lower the barrier height.[30]

2. Ohmic and Schottky contacts can be predicted qualitatively from the heats of reaction ΔH_R, such that the critical heat of reaction ΔH_{Rc} at 0.5 eV defines the

transition between reactive and unreactive metals and also low to high barrier heights.[30]

3. Silicides have been suggested to be more stable[31] because they form effective barriers to further interdiffusion at the interface. Furthermore the barrier heights can be expected to be scaled with their heats of formation.[32]

The results of the Phase I investigation follow.

3.0 Phase I Results

3.1 Phase I Technical Objectives

The development of ohmic and Schottky contacts is vital for the production of diamond devices. High contact resistances have been shown to limit the performance of diamond field effect transistors [33,34,35] and are rapidly becoming a problem for diamond-based photoconductive power switching.[36,37] Phase I was designed to demonstrate Schottky barrier height lowering and to electrically characterize the metal compound-diamond interface so that Phase II device fabrication objectives could be achieved. The metal-diamond interface has not been systematically characterized. Barrier heights (ϕ_B) and contact resistivities (R_C) of the different metals and silicides were examined as functions of implant doses and post-anneal temperatures. The Phase I program sought to answer the following questions:

1. Can ohmic contacts be formed using shallow silicon implantation into diamonds followed by annealing with metal to form a metal silicide/metal carbide diamond interface?

2. If ohmic contacts can be formed, how do the contact resistivities depend on implant doses, energies, and annealing temperatures?

3. What are the compositions of the interfaces as functions of implant doses, energies and annealing temperatures?

4. What Schottky behaviors can be realized if the interface is not ohmic? Is there a silicon carbide layer and can this layer be tailored to obtain a desired barrier height?

3.2 Phase I Experimental Results

3.2.1 Homoepitaxial Diamond Film Growth

All experiments were conducted using type IIa natural diamonds as substrates onto which doped epitaxial layers were deposited. Boron doped diamond films were grown on 2.5 mm x 2.5mm x 300 μm (100) oriented substrates using hot filament assisted chemical vapor deposition. The diamond substrates were cleaned in a saturated chromic acid solution at 160°C for 10 minutes followed by rinsing in a 1:1 solution of H_2O_2 in 30% NH_4OH at 70°C.[38] This cleaning procedure removes non-diamond carbon from the substrate surface. The substrate was then given a dip in concentrated HF to remove any metallic impurities left from the chromic acid solution. The substrate was given a final rinse in deionized water before being placed in the growth reactor. The diamond substrates were placed on a molybdenum holder in the diamond growth reactor 15 mm below a hot W filament heated to 2000°C. The reactor was pressurized to 12 torr with a flowing mixture of hydrogen, methane and diborane. The gas flow rates were 50 sccm of 1%methane in hydrogen, 35 sccm of hydrogen and 15 sccm

of 10 ppm diborane in hydrogen. The substrate temperature was approximately 850°C. The film growth was carried out for 1 hr producing a boron doped film ~1000 Å in thickness. The resistance between two tungsten probes 1mm apart on the surface of the doped film was ~400 kΩ. The Raman spectrum of the boron doped film is shown in Figure 1. This spectrum was taken using a glancing angle of incidence technique that gives results more characteristic of the near surface region. The spectrum is characteristic of diamond does not show any unusual Raman or photoluminescence features.

3.2.2 Silicon Ion Implantation

The Si implantation process required masking of the diamond substrate so that only selected regions were implanted. A SiO_2 film was used as the masking material to prevent the Si implant atoms from being deposited everywhere. A two layer mask set was used, one for defining the implantation areas and one for the metallization as shown in Figure 2. Figure 3 shows the detailed arrangement of the transmission line and Kelvin probe structures used for each metal. After diamond film growth, the diamond substrates were given another chromic acid cleaning to remove any non-diamond carbon residue from the film surface. It was observed that this chromic acid/HF cleaning step dramatically increased the diamond film resistance to a value of ~10^9 Ω between two tungsten probes spaced 1 mm apart. We believe that this increase was caused by chromic acid etching away of the boron doped epitaxial film. Following this cleaning, the SiO_2 mask was deposited by RF magnetron sputtering. The sputter conditions were 140 W at 13.6 MHz, 90 mtorr of Ar for 1.5 hrs. The substrate temperature increased to about 120°C at the end of the run. The SiO_2 film was ~4500Å thick. Each diamond substrate was divided into four sections called "Quads," see Figure 3. Three of the four quads were implanted with Si, each at a different dose, while one quad was never implanted but used as a control. Each of the three quads was sequentially implanted separately by opening up windows in the SiO_2 of the selected quad through photolithographic patterning and etching. Each quad had six (6) transmission line structures and six (6) Kelvin probes, one for each of the metals investigated, Pt, W, Ti, Ta, Mo, and Ni. Each of these structures was sequentially patterned onto the diamond and the metal deposited. All of the metals except Ti were deposited using DC sputtering. The Ti was e-beam evaporated. The metal thicknesses ranged from ~1500Å to ~4500Å. The Ni, W and Ta contacts showed severe adhesion problems and lifted off with removal of the photoresist metallization mask, and consequently only Pt, Ti and Mo were studied.

The implantation conditions were determined by carrying out a simulation of an implant using a program developed by Implant Sciences, Inc. The object of our approach was to use a near surface implant of Si so that it could react with the overlying metal film to produce a low resistance metal silicide contact region. Near surface implantation of Si into diamond requires the use of very low voltages as illustrated in the results of a simulation carried out for 15keV Si into diamond shown in Figure 4. The three curves are for different doses of Si, 10^{13}, 10^{14}, and 10^{15} 1/cm^2, that produce three different surface concentrations of Si. The Si implants were carried out by Implant Sciences, Inc.

3.2.3 Contact Annealing and Electrical Characterization

The I-V characteristics of the as-deposited contacts all showed very high resistances and nonlinear rectifying behavior. The sample was then annealed at 500°C in 30 mtorr of Ar for 20 minutes. Following this anneal, the contact resistance was still very high and the I-V characteristics were still nonlinear. The I-V characteristics are shown in Figures 5, 6 and 7 for Pt, Mo and Ti respectively. Each graph shows the I-V curves for each of the three Si implant doses and the control region that was not implanted. The I-V curves appear to be a combination of a reverse diode characteristic in series with a large resistance as illustrated in Figure 8. The series resistance consists of the contact resistance and the resistance of the boron doped epitaxial film, which in this case is substantial because the chromic acid cleaning procedure removed most of the boron doped film.

The Schottky barrier heights for the Pt, Ti and Mo contacts were measured using internal photoemission. The internal photoemission was measured by illuminating the region between two of the Kelvin probe pads with light from an Ar ion laser. The laser light was chopped by a variable speed chopper. The resulting photocurrent was detected by a lock-in amplifier that was connected to the Kelvin pads using two tungsten probes. The photoresponse of the contact was measured for eight different frequencies of the Ar laser. The photoresponse is proportional to the square of the barrier height according to

$$Y = B\left(h\nu - q\phi_B\right)^2 \qquad (5)$$

where B is a constant, h is Planck's constant, ν is the light frequency, q is the electronic charge and ϕ_B is the barrier height. Plotting the square root of the photoresponse versus photon energy, a linear plot is obtained with the barrier height given by the intercept at $Y^{1/2} = 0$. The square root of the measured photoresponse as a function of photon energy is shown in Figures 9, 10, and 11 for Pt, Ti and Mo contacts annealed at 500°C respectively. The four lines in each figure are for the three different Si implant doses and an unimplanted control. The barrier heights are nearly independent of the metal as evidenced by the nearly constant value of ~2 eV for the three control regions. The barrier height clearly decreases for the most heavily implanted contacts.

This data is more clearly presented in Figure 12 which shows the measured barrier height as a function of Si implant dose for each metal after the 500°C anneal. The barrier height appears to decrease more quickly for those metals which form silicides at lower temperature indicating that metal silicide formation may be taking place. The barrier heights were also measured after annealing at 1000°C and are shown in Figure 13 as a function of the Si implant dose. The barrier heights have decreased only slightly from their values at the 500°C anneal, this may be due to the fact that the metal has fully reacted with the Si implant at 500°C. We also measured the specific contact resistivity using the 80μm x 80μm Kelvin structures after the 1000°C anneal. The specific contact resistivity is shown for the Pt and Mo contacts as a function of Si implant dose in Figure 14 for several different sets of contact pads.

The greatest amount of scatter occurs for the implant done at 10^{14} cm^{-2} and the unimplanted contacts. The reason for the scatter we believe is that a misalignment of the mask occurred during patterning for metallization. The misalignment was greatest for the quads B and D which correspond to the 10^{14} and unimplanted contacts. The misalignment causes an error in the actual contact area because the metal contact area no longer fully covers the implant area. The contact misalignment has no effect on the barrier height measurements of Figures 9 - 13.

The large values for the specific contact resistances are primarily due to the low level of boron doping in the diamond film. Recall from earlier that the boron doped epitaxial film had a resistance of ~400kΩ just after film growth and that a chromic acid etch was used to clean the film surface just before implantation. The chromic acid etch apparently etches the diamond as well as graphitic carbon but at a much lower rate. After the chromic acid etch, the resistance between two tungsten probes spaced 1 mm apart was ~10^{9}Ω. If we assume that approximately 500 Å of the doped film remains, the resistivity of the diamond surface would be ~10^{12} Ω-cm, and thus the number of acceptors, Na, is very small. Under such low doping conditions, the contact resistance, Rc, will be determined by thermionic emission so that Rc is determined by the barrier height. However if we had a higher concentration of acceptors then Rc is determined by field emission processes for which $\log(Rc) \sim \phi_B/(Na)^{1/2}$. Thus Rc can be further lowered by heavily doping the contact area. Our high values of specific contact resistivity are an artifact of the fact that we inadvertantly etched away part of our boron doped epilayer by the use of a commonly adopted chromic acid cleaning procedure. Thus the observed reductions in barrier height and specific contact resistivity are all the more significant. If the experiments were to be conducted using diamond films doped ~10^{6}-10^{10} times greater than in this study, that is resistivities on the order of 10^{2} - 10^{4} Ω-cm, the specific contact resistance would decrease by an additional ~10^{3}-10^{5} times or specific contact resistivities would be about 10^{-2} - 10^{-4} Ω-cm^2. Thus optimization of the Si implant dose combined with co-implantation of boron along with the Si for p-type materials could lead to substantially reduced contact resistances.

3.3 Conclusions

We discovered that Pt and Ti contacts to shallow silicon implants in diamond become ohmic upon annealing to 500°C. We have also demonstrated for the first time lowering of the Schottky barrier height of Pt and Ti metal contacts on very lightly doped diamond through the use of a novel shallow Si implant and annealing method. Implantation of 10^{15} Si /cm^2 at 15 keV followed by annealing at 500°C causes a reduction of the Schottky barrier height by a factor of two in the case of Pt and a 35% reduction for Ti metallization. There was very little change in the barrier height for Mo contacts even at annealing temperatures ~1000°C. The amount of the barrier lowering is proportional to the metal silicide formation temperature. The larger the implanted dose of Si, the greater the degree of barrier lowering. This is an important observation and points the way for further development of this approach.

References

1 R. F. Davis, Z. Sitar, B. E. Williams, H. S. Kong, H. J. Kim, J. W. Palmour, J. A. Edmond, J. Ryu, J. T. Glass and C. H. Carter, Jr., Mat. Sci. Eng., **B1**, 77 (1988).

2 H. Shiomi, H. Nakahata, T. Imai, Y. Nishbayashi and N. Fujimori, Jap. J. Appl. Phys. **28**, 758 (1989).

3 K. Shenai and B. J. Baliga, Proc. First Int'l Symp. Diamond and Diamond-like Films, Electrochemical Soc. Proceedings, **89-12**, 405 (1989).

4 K. L. Moazed, J. R. Zeidler and M. J. Taylor, J. Appl. Phys. **68**, 2247 (1990).

5 K. L. Moazed, J. R. Zeidler, M. J. Taylor and C. A. Hewett, Diamond and Diamond-like Films and Coatings, Plenum Press, NATO Advanced Study Institute Publication Series (1991).

6 K. L. Moazed, J. R. Zeidler and M. J. Taylor, Mat. Res. Soc. Symp. Proc. **162**, 347 (1990)

7 F. Fang, C. A. Hewett, M. G. Fernandes and S. S. Lau, IEEE Trans. Elect. Dev. **36**, 1783 (1989).

8 Yu. M. Rotner, N. N. Golembievskii, L. F. Litovchenko, N. N. Kubenskaya, and V. A. Presnov, Prib. Tekh. Eksp. **1**, 226, (1975).

9 K.L. Moazed, Richard Nguyen, J.R. Zeidler, IEEE Elec. Dev. Lett., **9**, 350, (1988).

10 Hiromu Shiomi et al, Jap. Journal of Appl. Physics, **28**, 758, (1989)

11 A.T. Collins, E.C. Lightowlers, P.J. Dean, Phys. Rev. **183**, 725 (1969)

12 A.T. Collins, E.C. Lightowlers, P.J. Dean, Diamond Res. 19, 1970

13 M. Drake, W.J. Leivo, Phys. Rev., 111(5), Sept 1958

14 R.H. Wentorf, M.P. Bovenkerk, J. Chem. Phys., 36, 1987 (1962).

15 S.M. Sze, Physics of Semiconductor Devices, 2nd Edition (1981).

16 G. S. Sandu, M. L. Swanson and W. K. Chu, Appl. Phys. Lett. **55**, 1397 (1989).

17 B. Liu, G. S. Sandhu, N. R. Parikh and M. L Swanson, Nucl. Inst. Meth.Phys Res. **B45**, 420 (1990).

18 G. H. Glover, Solid St. Elect. **16**, 973 (1973).

19 C. A. Mead and T. C. McGill, Physics Lett., **58**, 249 (1976).

20 F. J. Himpsel, D. E. Eastman and J. F. van der Veen, J. Vac. Sci. Technol., **17**, 1085 (1980).

21 M. C. Hicks, C. R. Wronski, S. A. Grot, G. Sh. Gildenblat, A. R. Badzian, T. Badzian and R. Messier, J. Appl. Phys. **65**, 2139 (1989).

22 C. P. Beetz, Jr., B. A. Lincoln and D. R. Winn, SPIE Proc. Diamond Optics III **1325**, 240 (1990).

23 CRC Handbook of Chemistry and Physics, 68th edition

24 I .J. Brillson, J. Phys. Chem. Solids, **44** , 703 (1983).

25 F. Fang, C. A. Hewett, M. G. Fernandes and S. S. Lau, IEEE Trans. Elect. Dev. **36**, 1783 (1989).

26 Eric A. Brandes, editor, Smithells Metals Reference Book, 6th edition, 8-1 to 8-62 (1983)

27 CRC Handbook of Chemistry and Physics, 68th edition

28 J.M. Andrews, J.C. Phillips, Phys. Rev. Lett., 35, p56, (1975)

29 O. Kubaschewski, C.B. Alcock, Metallurgical Thermochemistry, 5th ed., p 268-323, Pergamon Press (1977)

30 L.J. Brillson, J. Phys. Chem. Solids, 44 (8), p 703, (1983)

31 R. Kaplan, R.J. Wagner, H.J. Kim, R.F. DAvis, Solid State Commun., 55, p67, (1985)
32 J.M. Andrews, J.C. Phillips, Phys. Rev. Lett., 35, p56, (1975)
33 G. Sh. Gildenblat, S. A.Grot, C. W. Hatfield, and A. R. Badzian, IEEE Elect. Dev. Lett., 12, 37 (1991).
34 S. Hiromu, Y. Nishibayashi, and N. Fujimori, Jap. J. Appl. Phys., 28, L2153 (1989).
35 C. R. Zeisse, C. A. Hewett, R. Nguyen, J. R. Zeidler, and R. G. Wilson, IEEE Elect. Dev. Lett., 12, 602 (1991).
36 S. Feng, P. T. Ho, and J. Goldhar, IEEE Trans. Elect. Dev., 37, 2511 (1990).
37 C. P. Beetz, and R. Tayrani, Quarterly Progress Report, "Development of Dopant Modulated Single Crystal Diamond Film Photoconductive Switch," SDIO Contract #DASG60-90-C-0155, Feb. 1991-April 1991.
38 G. Sh. Gildenblat, S. A. Grot, C. W. Hatfield, C. R. Wronski, A. R. Badzian, T. Badzian, and R. Messier, Mat. Res. Bull., 25, 129 (1990).

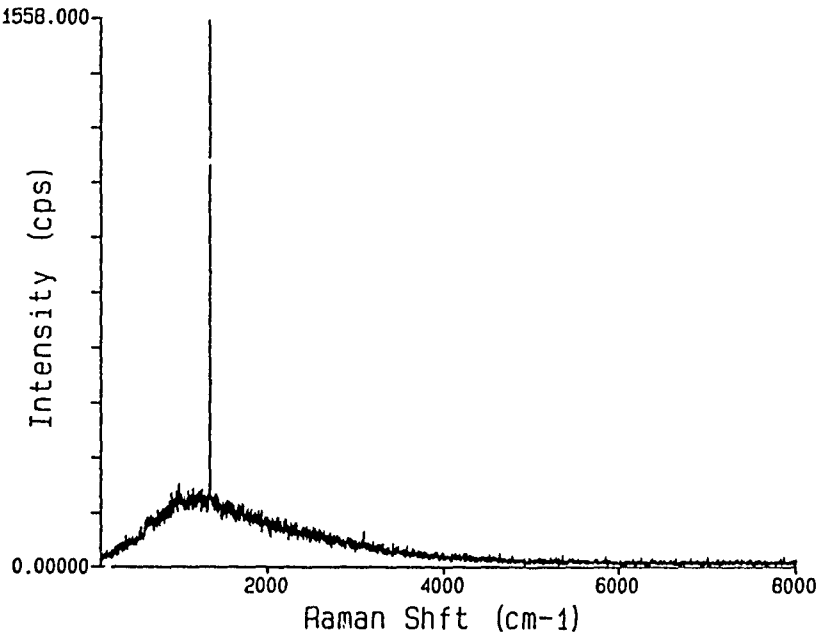
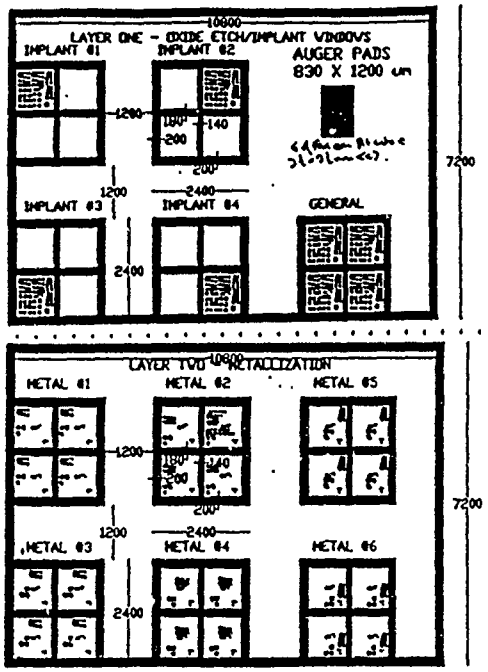
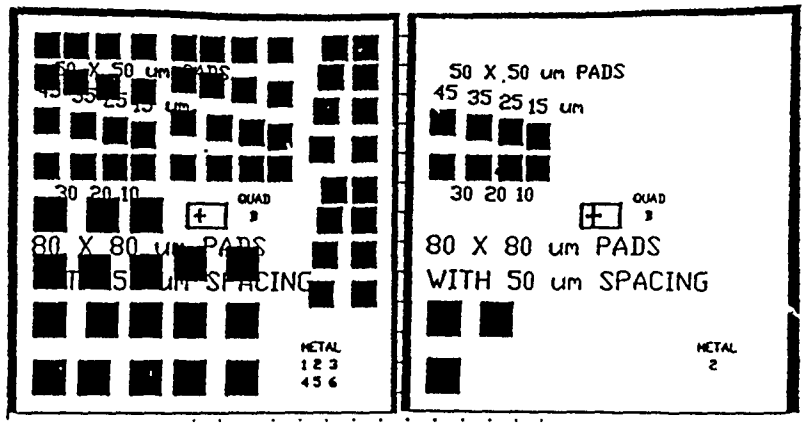


Figure 1. Raman spectrum of boron doped homoepitaxial diamond film on type IIa natural diamond. The spectrum was excited using a glancing angle of incidence for the Ar laser light so that more of the near surface region was sampled.



MASK LAYOUTS FOR IMPLANTED CONTACTS
Layer One is for the oxide etch and implant mask.
Layer Two is for the metal mask.

Figure 2. Two layer mask used to define the implant and metallization areas.



Enlargement of one quad of Layer One and Layer Two.
Eight pads are used for transmission line measurements for contact R.
Three pads are used for Kelvin measurement of contact R. the same 3 pads (any two pads of similar metals) can be used for measuring photoresponse barrier heights.

Figure 3. Details of the mask showing transmission line and Kelvin probe structures and dimensions.

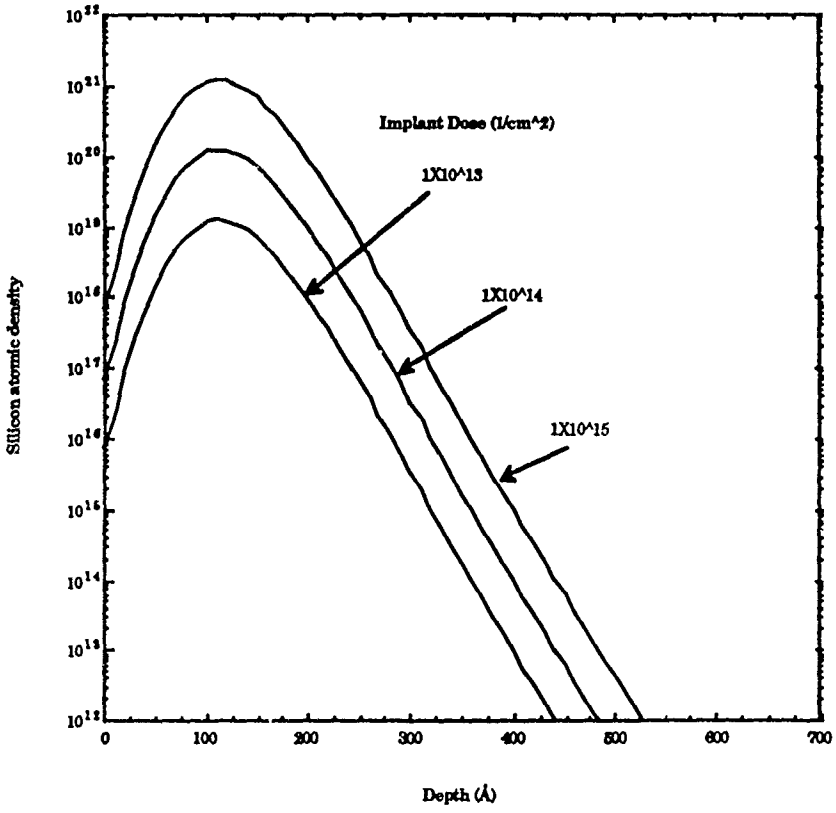


Figure 4. Simulated Si implant depth profiles in diamond at 15keV accelerating voltage.

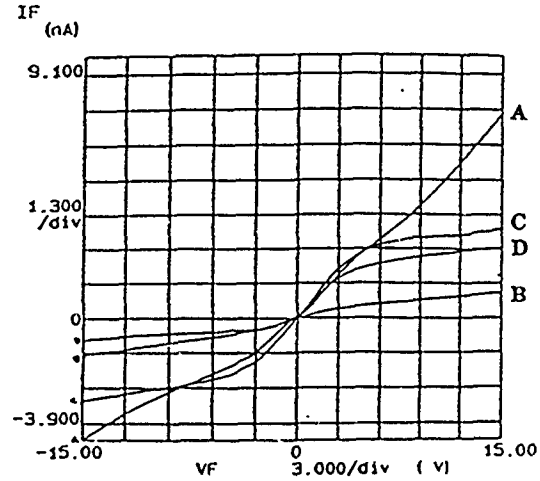


Figure 5. Current versus voltage for Pt metal on 15 keV Si implanted and unimplanted regions annealed at 500°C. Implant dose notation: A - 10^{13} cm^{-2}, B - 10^{14} cm^{-2}, C - 10^{15} cm^{-2}, D - no implant.

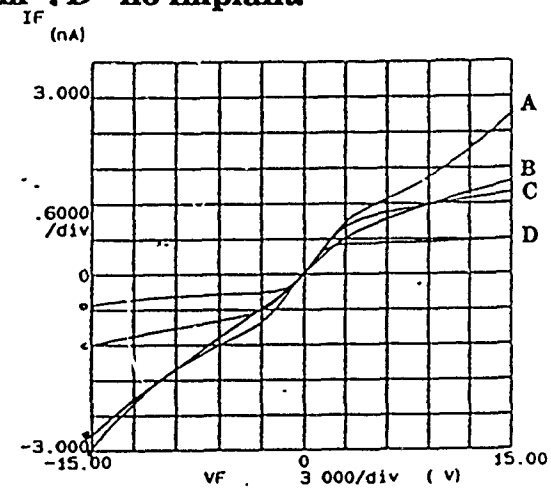


Figure 6. Current versus voltage for Mo metal on 15 keV Si implanted and unimplanted regions annealed at 500°C. Implant dose notation: A - 10^{13} cm^{-2}, B - 10^{14} cm^{-2}, C - 10^{15} cm^{-2}, D - no implant.

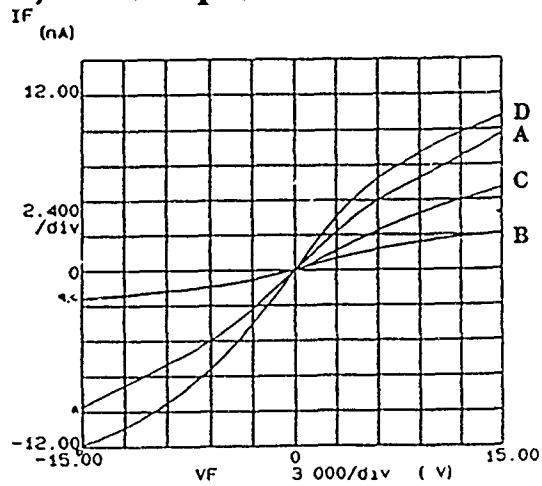


Figure 7. Current versus voltage for Ti metal on 15 keV Si implanted and unimplanted regions annealed at 500°C. Implant dose notation: A - 10^{13} cm^{-2}, B - 10^{14} cm^{-2}, C - 10^{15} cm^{-2}, D - no implant.

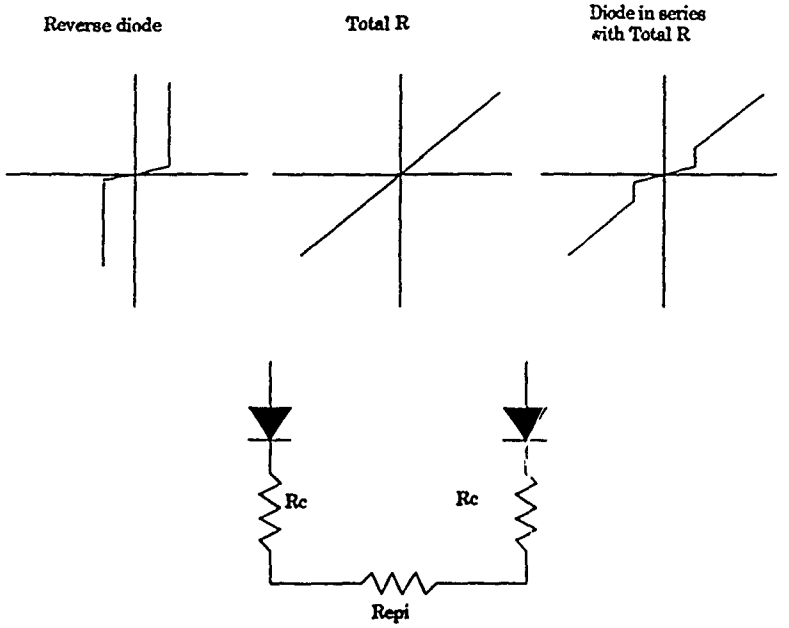


Figure 8. Schematic illustrating the effect of the contact and diamond film series resistances on the I-V characteristic.

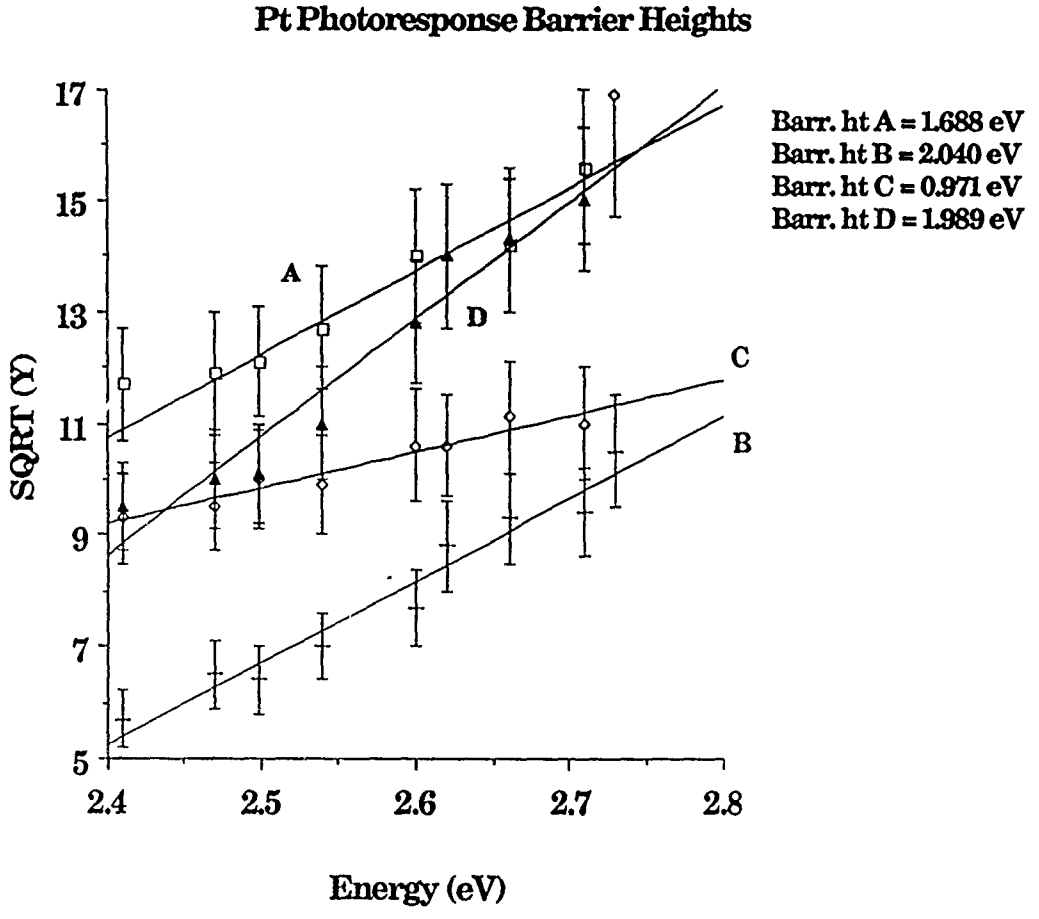


Figure 9. Barrier heights of Pt contacts on 15keV Si implanted and unimplanted regions annealed at 500°C. The implant dose notation is the same as in Figures 5, 6, and 7.

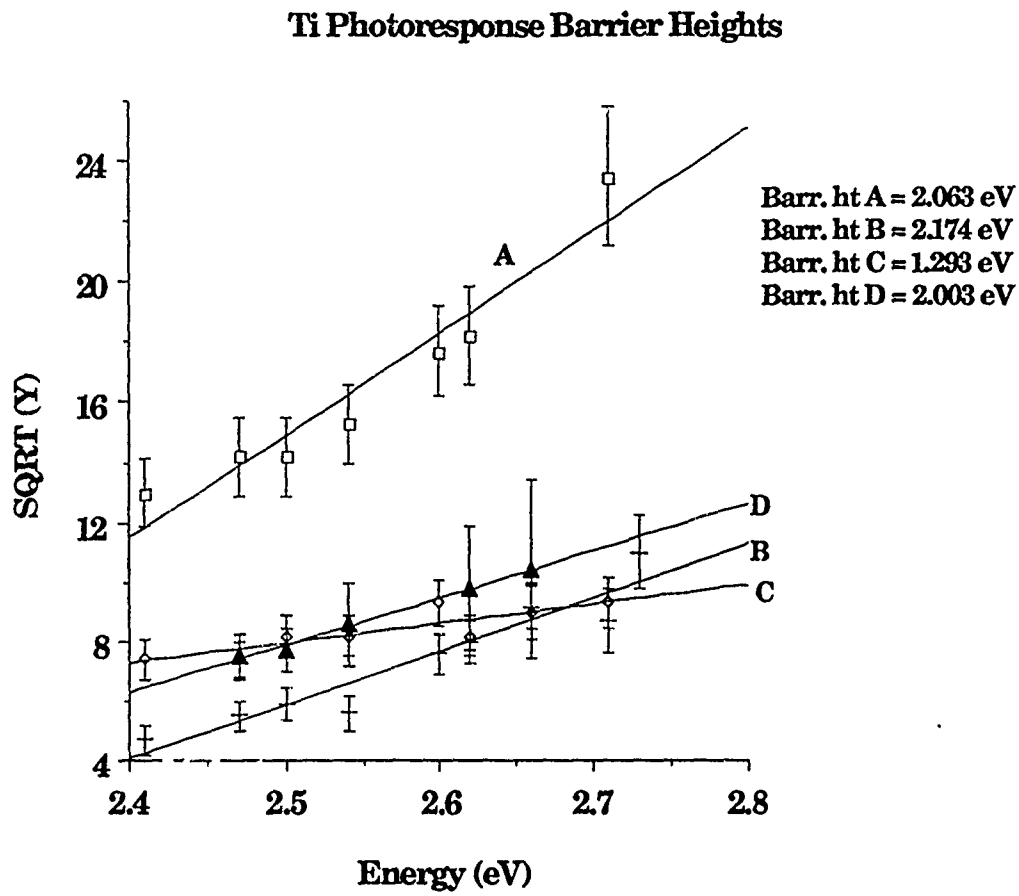


Figure 10. Barrier heights of Ti contacts on 15keV Si implanted and unimplanted regions annealed at 500°C. The implant dose notation is the same as in Figures 5, 6, and 7.

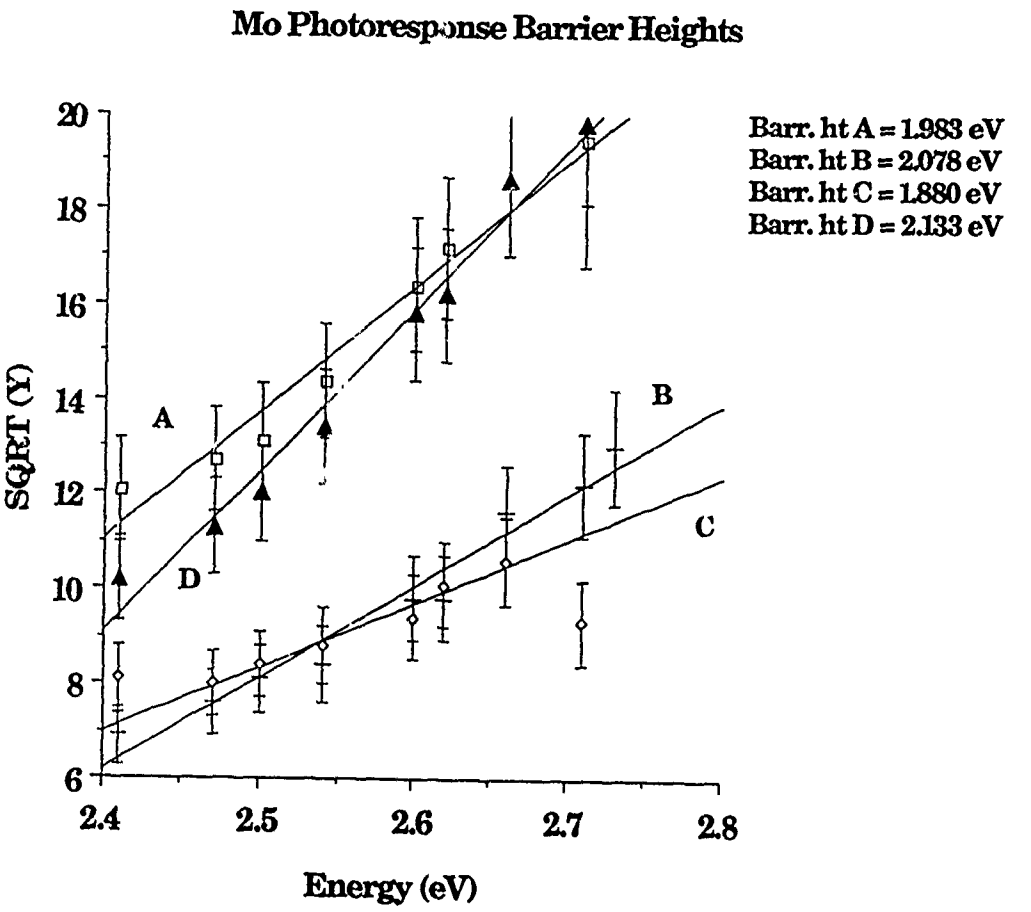


Figure 11. Barrier heights of Mo contacts on 15keV Si implanted and unimplanted regions annealed at 500°C. The implant dose notation is the same as in Figures 5, 6, and 7.

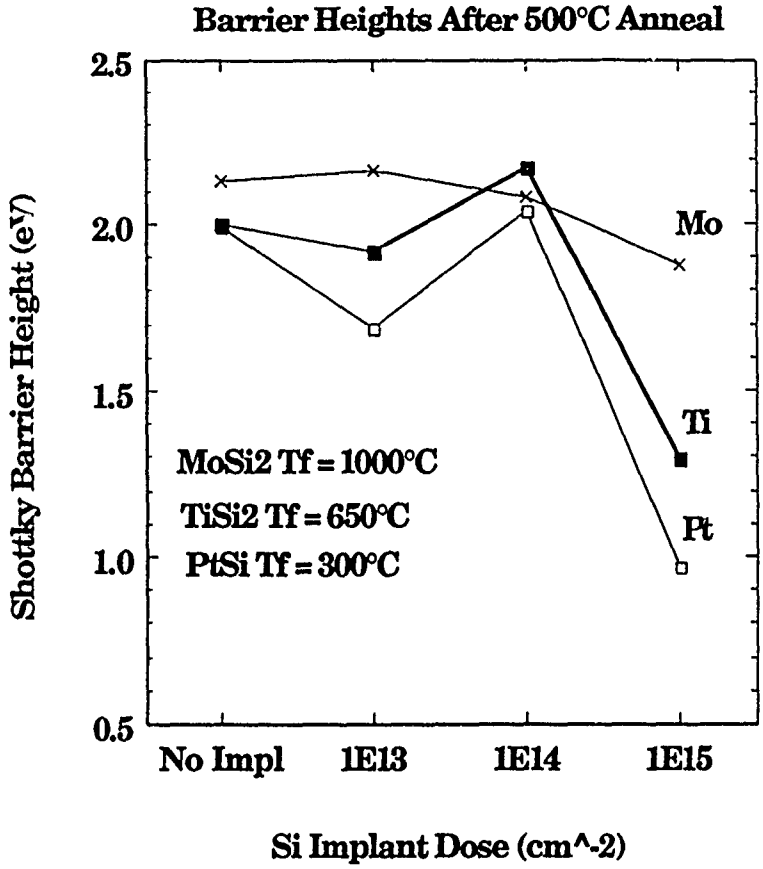


Figure 12. Schottky barrier heights as a function of Si implant dose for Pt, Ti and Mo contacts after 500°C anneal. The metal silicide formation temperature is also shown.

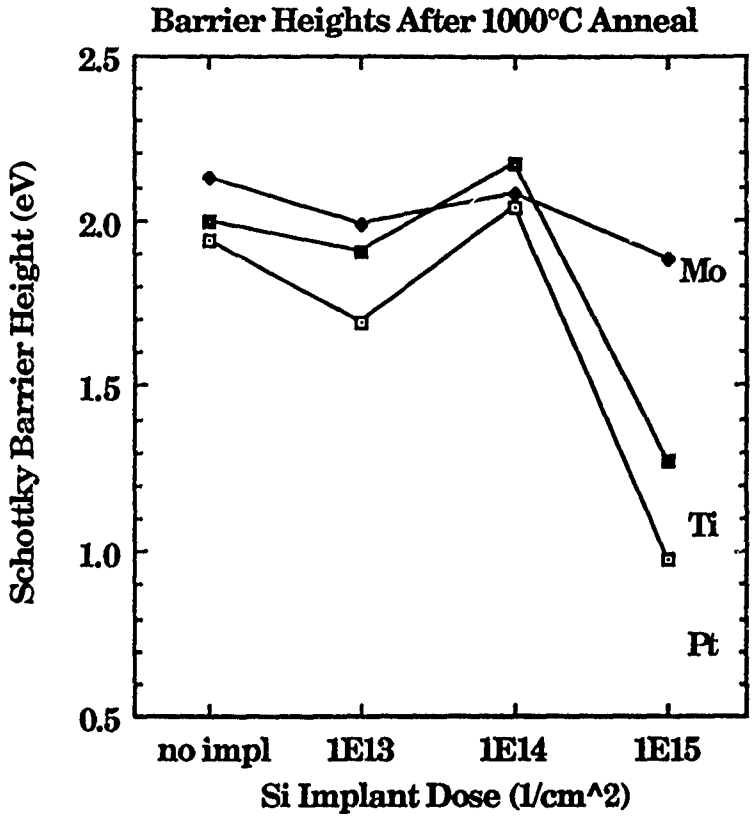


Figure 13. Schottky barrier heights as a function of Si implant dose for Pt, Ti and Mo contacts after annealing at 1000°C. The barrier heights have decreased slightly more than at the 500°C anneal.

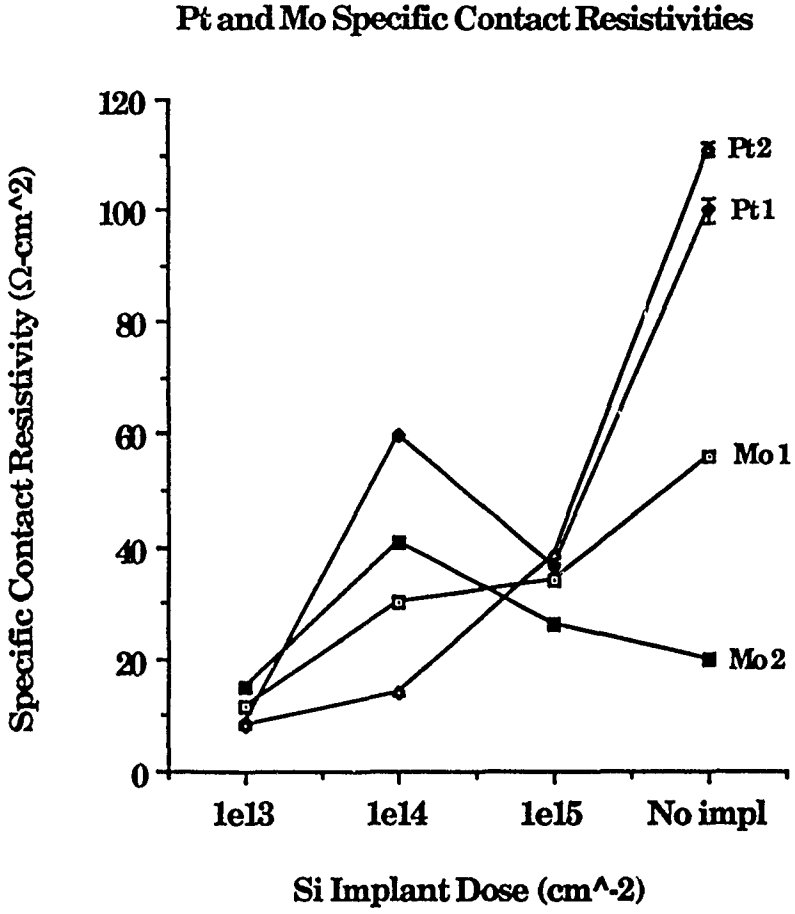


Figure 14. Specific contact resistivity as a function of Si implant dose following annealing at 1000°C. Note that these values are large primarily due to the fact that the underlying boron doped film has been almost entirely etched away by the chromic acid etch just prior to the Si implantation. We estimate the surface resistivity of the diamond at ~10^{12} Ω-cm.

SUPPLEMENTARY

INFORMATION

Advanced Technology Materials, Inc.
7 Commerce Drive, Danbury, CT 06810 (203) 794-1100 FAX (203) 792-8040

July 15, 1992

To: Distribution

U. S. Army Strategic Defense Command
P. O. Box 1500
Huntsville, AL 35807-3801

CCSD-AT-P (Mr. Martin)
CSSD-AJ-S
CSSD-CM-C
CSSD-IM--PA
ONR Office of Naval Research
Code 1114
ATTN: Mr. Max Yoder
Arlington, VA 22217-5000
DTIC Defense Technical Information Center
Cameron Station
Alexandria, VA 22314
ARO U. S. Army Research Office
ATTN: SLCRO-EL/Dr. M. Stoscio
P. O. Box 12211
Research Triangle Park, NC

From: Advanced Technology Materials, Inc.
7 Commerce Drive
Danbury, CT 06810

Re: Final Report and Special Technical Summary Covers
Contract DASG60-91-C-0025

Enclosed are revised Cover sheets. Please locate the Final Report and Special Technical Summary and replace the existing cover pages with the ones provided.

Thank you.

Duncan W. Brown
Vice President
Advanced Technology Materials, Inc.
7 Commerce Drive
Danbury, CT 06810

IMPLANTED CONTACTS FOR DIAMOND SEMICONDUCTOR DEVICES

FINAL REPORT

CONTRACT
DASG60-91-C-0025

SPONSORED BY

U. S. ARMY STRATEGIC DEFENSE COMMAND

CONTRACT PERIOD
2/12/91 TO 11/12/91

Soo Hee Tan and C. P. Beetz, Jr.
Principal Investigators
(203-794-1100)

ADVANCED TECHNOLOGY MATERIALS, INC.
7 COMMERCE DRIVE
DANBURY, CT 06810